

[Electrochemistry]

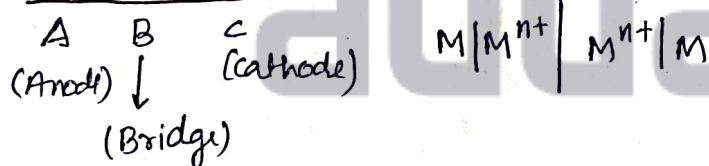
• INTRODUCTION

Electrochemistry is study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring non-spontaneous transformation.

• DIFFERENCE between Electrochemical & Electrolytic cell

- | Galvanic cell
Electrochemical cell | Electrolytic cell |
|---|---|
| • Converts chemical energy to electrical energy. | • Converts electric energy to chemical energy. |
| • Cathode is positive electrode and anode is negative electrode | • Anode is positive electrode and cathode is negative electrode |
| • Oxidation takes place at anode, reduction takes place at cathode. | • Oxidation occurs at anode and reduction occurs at cathode. |
| • Salt bridge present | • Salt bridge absent |
| • Application in battery | • Application in purifying copper |

• Representation of cell



$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} \\ = E_{\text{cathode}} - E_{\text{anode}}$$

• Standard Hydrogen Electrode

Representation: $\text{Pt}(s) | \text{H}_2(g) (1 \text{ bar}) | \text{H}^+(aq) (1 \text{ M})$

half cell equation: $\text{H}^+(aq) + e^- \rightarrow \frac{1}{2} \text{H}_2(g)$

$$E^\circ_{\text{SHE}} = 0$$

• Nernst Equation

$$E_{\text{cell}} = E^\circ - \frac{2.303 RT}{nF} \lg \frac{[\text{Product}]}{[\text{Reactant}]}$$

At 298 K

$$E_{\text{cell}} = E^\circ - \frac{0.0591}{n} \lg \frac{[\text{Product}]}{[\text{Reactant}]}$$

• Relation between E° and K_{eq} and At equilibrium,

$$E_{\text{cell}} = 0, \quad \frac{[\text{Prod}]}{[\text{React}]} = K_{\text{eq}}$$

$$E_{\text{cell}} = E^\circ - \frac{0.0591}{n} \lg \frac{[P]}{[R]}$$

$$0 = E^\circ - \frac{0.0591}{n} \lg K_{\text{eq}}$$

$$\lg K_{\text{eq}} = \frac{nE^\circ}{0.0591}$$

$$K_{\text{eq}} = 10^{\frac{nE^\circ}{0.0591}}$$

• Relation between ΔG° and E°

$$\Delta G^\circ = -nFE^\circ$$

$\downarrow$ Standard Gibbs free energy
 $\downarrow$ no. of electrons
 $\downarrow$ Faraday const. (96500 C)

• Conductance

$$\text{Resistance (R)} = \frac{\rho l}{a}$$

$$\text{Resistivity (}\rho\text{)} = \frac{Ra}{l}$$

$$\text{Conductance (G)} = \frac{1}{R} = \frac{1}{\rho} \frac{a}{l}$$

$$= \frac{Ka}{l}$$

$$\text{Conductivity (K)} = \frac{1}{\rho}$$

$$= \frac{Gl}{a}$$

• SI units

$$\text{Resistance} = \Omega$$

$$\text{Resistivity} = \Omega \text{ m}$$

$$\text{Conductance} = \text{S}$$

$$\text{Conductivity} = \text{S m}^{-1}$$

$$\text{cell constant} = \frac{\text{length}}{\text{Area}}$$

$$G^* = \frac{l}{a}$$

$$\text{SI unit} = \text{m}^{-1}$$

Ayushi Sharma

• Factors on which conductivity depends

Conductivity: (κ)

It is conductance of one unit volume of a solution kept between two platinum electrodes with unit area of cross section and at distance of unit length.

Molar Conductivity: (λ_m)

It is conductance of volume (V) of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length.

• Concentration dependance

• Conductivity always decreases with increase in concentration both for strong and weak electrolytes.

• Molar conductivity increases with decrease in concentration.

• When concentration approaches zero, the molar conductivity is known as limiting molar conductivity (λ_m°)

• Kohlrausch law

Limiting molar conductivity of an electrolyte can be represented as sum of the individual contribution of anion and cation of the electrolyte.

$$\lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

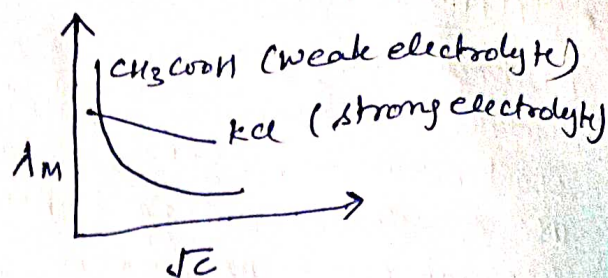
λ_m° for weak electrolyte is obtained using Kohlrausch law

$$\text{Degree of dissociation } (\alpha) = \frac{\lambda_m}{\lambda_m^\circ}$$

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C\lambda_m^2}{\lambda_m^\circ(\lambda_m^\circ - \lambda_m)}$$

$$\lambda_m = \lambda_m^\circ - A\sqrt{C} \rightarrow (\text{Concentration})$$

↓
limiting molar conductivity
Molar conductivity
for strong electrolyte

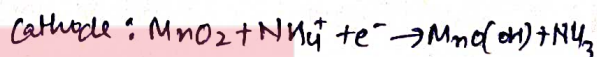
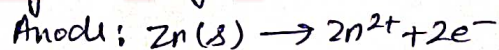


• First law: Amount of chemical reaction which occurs at any electrode is proportional to quantity of electricity passed.

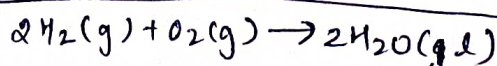
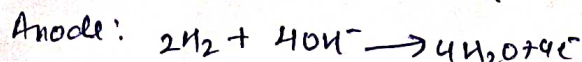
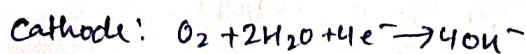
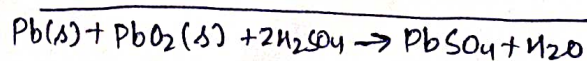
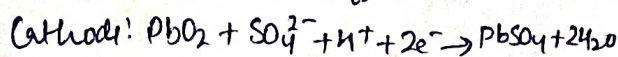
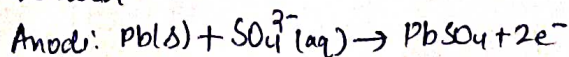
• Second law: Amount of different substance liberated by same quantity of electricity is proportional to their chemical equivalents

Product of electrolysis depend on different oxidising and reducing species present in electrolytic cell and their standard electrode potentials.

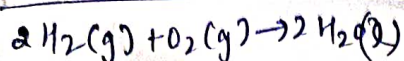
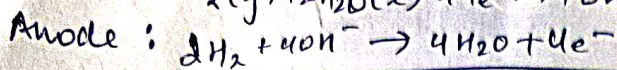
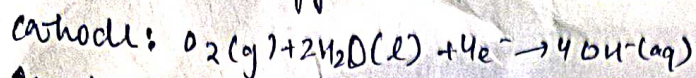
In primary battery, reaction occurs only once. They cannot be reused.



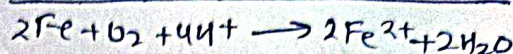
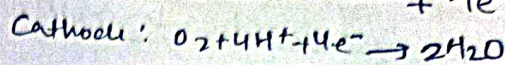
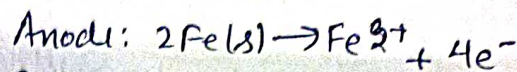
In secondary cell, it can be recharged by passing current through in opposite direction so that can be reused.



Galvanic cell that are designed to convert the energy of combustion of fuels like hydrogen, methane directly into electrical energy are called fuel cells.



Corrosion, slowly coats the surface of metallic objects with oxides or other salts of the metal.



[Chemical Kinetics]

• Introduction

Rate of reaction can be defined as change in concentration of a reactant or product in unit time.

$$\text{Rate} = \frac{[\Delta \text{conc}]}{[\Delta \text{time}]}$$

• Rate of Reaction

Average rate of reactant reaction = $\frac{-\Delta R}{\Delta t} = \frac{\Delta P}{\Delta t}$

Instantaneous rate of reaction = $\frac{-dR}{dt} = \frac{dP}{dt}$

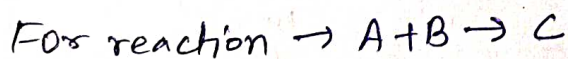
• Unit of rate

Unit of rate = $\text{conc.} \cdot \text{time}^{-1}$
 $= M L^{-1} \text{time}^{-1}$

• Rate Law

Rate of Reaction $\propto [\text{conc of reactant}]^x$

Rate = $k [\text{Reactant}]^x$



Rate = $k [A]^x [B]^y$

where x and y are not stioichiometry

• Order of reaction

The sum of powers of the concentration of the reactants in rate law expression is called the order of that chemical reaction.

• order of reaction can be 0, 1, 2, or any fraction

• Molecularity

No. of reacting species taking part in elementary reaction are called molecularity of reaction.

• Complex reaction

The reactions in which no. of reacting species is more than 03. Such reactions cannot occur in single step and occur in multiple steps. The slowest step among steps is known as rate determining step and that step gives order of reaction.

• Zero Order reaction

$[A] = [A_0] - kt$

where $[A]$ = conc. of reactant at time t .

$[A_0]$ = conc. initial.

k = rate constant

t = time.

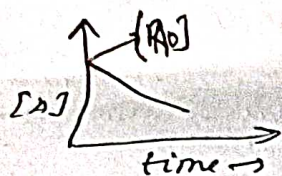
• First order reaction

$\ln[A] = \ln[A_0] - kt$

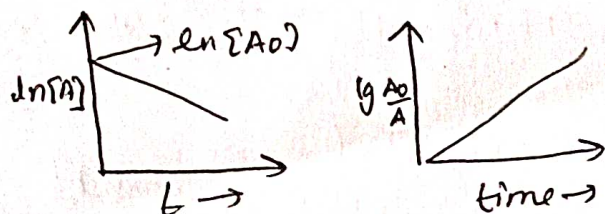
$[A] = [A_0] e^{-kt}$

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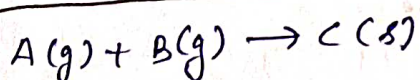
• Graph for zero order reaction



• Graph for first order reaction



• First order reaction in terms of pressure



$$k = \frac{2.303}{t} \lg \frac{P_i}{2P_i - P_t}$$

where P_i = Initial Pressure of gas A

P_t = total Pressure at time t

• Half life of Reaction

Half life is the time in which conc. of reactant is reduced to one-half.

It is represented by $t_{1/2}$

• Half life for zero order reaction

$$t = t_{1/2} \quad A = A_0$$

$$t_{1/2} = \frac{[A_0]}{2k} \rightarrow \text{Initial conc. of A}$$

$2k \rightarrow \text{Rate constant.}$

• Half life for first order reaction

$$t = t_{1/2} \quad A = A_0$$

$$t_{1/2} = \frac{0.693}{k} \rightarrow \text{Rate constant}$$

• Pseudo order first order reaction

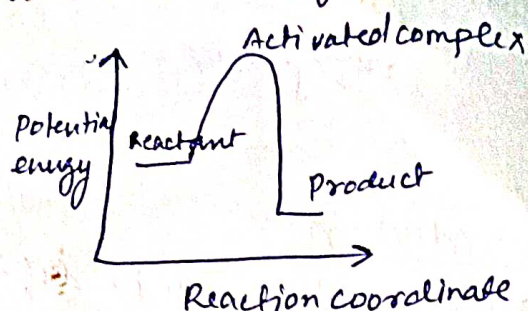
The reaction which obey first order rate law although they are higher order reactions. Such reactions are called pseudo first order reaction.

• Arrhenius equation

This equation gives the relation of rate constant with temperature.

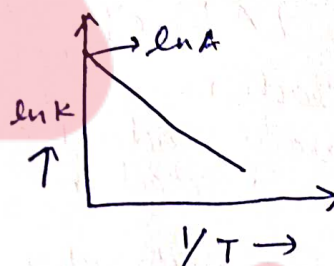
$$k = A e^{-E_a/RT}$$

where A is Arrhenius or frequency factor. R is the gas constant and E_a is the activation energy.



• Graph for Arrhenius eqⁿ

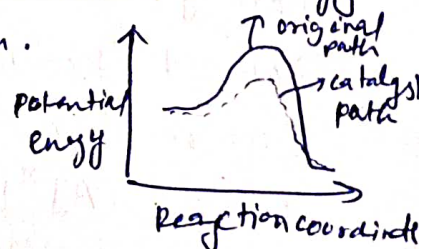
$$\ln k = -\frac{E_a}{RT} + \ln A$$



• For two temperatures

$$\lg \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

Catalyst → A substance that enhances rate of reaction by lowering the activation energy of reaction.



• Collision theory

It states that only those collisions are effective collision which have enough activation energy and proper orientation of molecules.

[SURFACE CHEMISTRY]

ADSORPTION

Introduction

The accumulation of molecular species at surface rather than in bulk of a solid or liquid is known as adsorption.

For concentration (solⁿ phase)
Extent of adsorption & Concentration of solution

$$\frac{x}{m} = k c^{1/n}$$

Lyophilic & Lyophobic sols

- | Lyophilic Sol | Lyophobic Sol |
|---|--|
| <ul style="list-style-type: none"> • Lyophilic means colloids that are liquid loving. • They are also called reversible sols. • These sols are quite stable. | <ul style="list-style-type: none"> • Lyophobic means colloids that are liquid hating. • They are also called irreversible sols. • They need stabilizing agent for preservation. |

Multimolecular & Macromolecular sols

- On dissolution, a large number of atoms or smaller particles aggregate together to form species having size in colloidal range.
- For eg. gold sol, sulphur sol etc.

- Macromolecules in suitable solvents form solutions in which the size of macromolecules may be in colloidal range.
- For eg. starch, cellulose, nylon etc.

Associated Colloids →

Substances which at lower concentration behave as normal electrolytes but at higher conc. exhibit colloidal behavior due to formation of aggregates is known as associated colloids.

The formation of micelle takes place only above particular temperature known as Krafft Temperature (T_k) and only above specific concentration known as critical micelle concentration.

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Sorption →

When both adsorption and absorption takes place simultaneously then it is called sorption.

Desorption →

The process of removing an adsorbed surface/substance from a surface on which is adsorbed is known as desorption.

Mechanism of Adsorption →

- Due to Residual forces
- With increase in surface area, adsorption extent also increases
- Heat of adsorption

$$\Delta H = -ve, \quad \Delta S = -ve$$

$$\text{for } \Delta G = -ve, \quad \Delta H > T\Delta S$$

$$\text{for equilibrium, } \Delta H = T\Delta S$$

Difference between physisorption & chemisorption

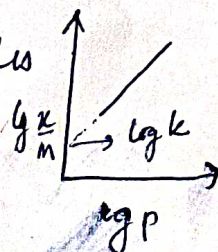
- | Physisorption | Chemisorption |
|---|--|
| <ul style="list-style-type: none"> • involves van-dur Waals forces • ^{not} Specific in nature • Reversible • Low enthalpy of adsorption. • Results in multi-molecular layer | <ul style="list-style-type: none"> • involves chemical bonding • highly specific in nature. • Irreversible • High enthalpy of adsorption. • Results in uni-molecular layer. |

Freundlich Adsorption isotherm

$$\text{Extent of adsorption } \frac{x}{m} = k p^{1/n}$$

Taking log on both sides

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$



Tyndall effect

Colloidal solutions if it observed from a direction at right angle to the direction of light beam, it appears perfectly dark. Thus when viewed at right angles to the passage of light i.e. the path of the beam is illuminated by bluish light. This is known as Tyndall effect.

Condition

- Diameter of dispersed particles is much smaller than wavelength of light used.
- Refractive index of dispersed phase and dispersion medium differ gently in magnitude.

Brownian movement

When colloidal particles viewed under ultramicroscope, colloidal particles appear to be in state of continuous zig-zag motion. This motion is known as brownian movement.

Electrophoresis

Existence of colloidal particles having charge is confirmed by electrophoresis experiment.

The movement of colloidal particles under an applied electric potential is called electrophoresis.

If somehow, the charge is removed from colloidal particles, the particles will come nearer to each other to form aggregates. This process is called coagulation or precipitation of sols.

Coagulation

Coagulation can occur by :

- ① electrophoresis
- ② By mixing two oppositely charged sol
- ③ By boiling
- ④ By persistent dialysis
- ⑤ By addition of electrolytes

Hardy Saultz rule

Greater the valency of flocculating ion added, the greater is its power to cause precipitation.

Emulsions

If a mixture of two miscible or partially miscible liquids is shaken a coarse dispersion of one liquid in other is obtained which is called emulsion.

Oil dispersed in water

- They are unstable
- For stabilizing of emulsion emulsifying agents are added.
- eg milk, liq. fat

Water dispersed in water

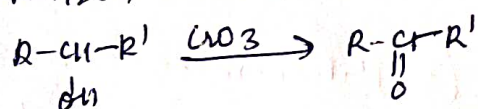
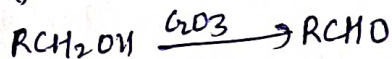
- oil acts as dispersion medium.
- eg - butter, cream.

ALDEHYDE, KETONE, CARBOXYLIC ACIDS

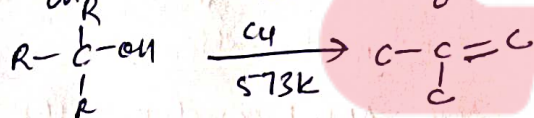
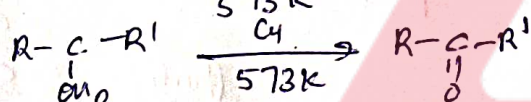
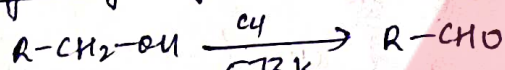
- Carbon atom is sp^2 hybridised.
- The fourth valence electron of carbon remains in p-orbital and forms π bond with oxygen while three valence electrons form 3 σ bonds.

Preparation of aldehydes & ketones

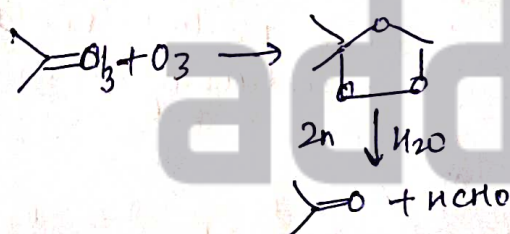
① By oxidation of alcohols



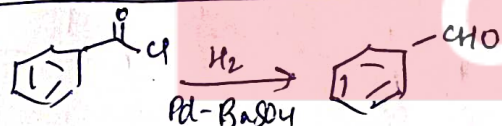
② By dehydrogenation of alcohols



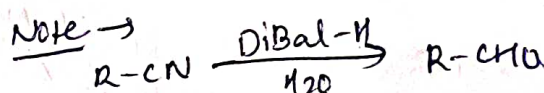
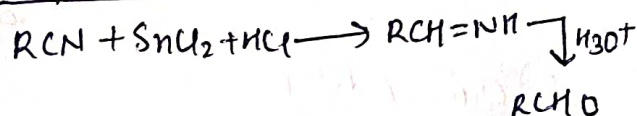
③ From hydrocarbons (ozonolysis)



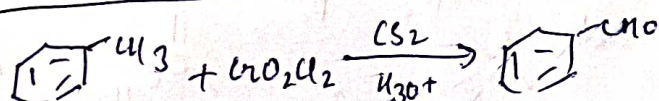
① Rosenmund Reduction



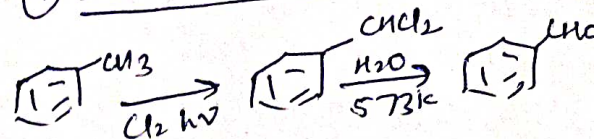
② Stephen Reaction



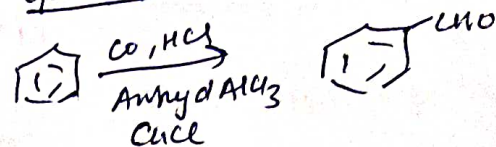
③ Etard Reaction



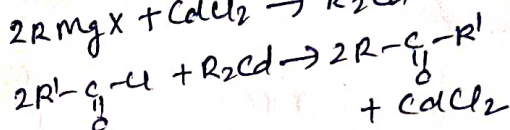
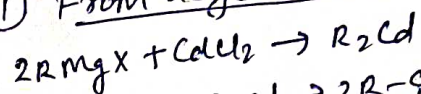
④ Side chain chlorination



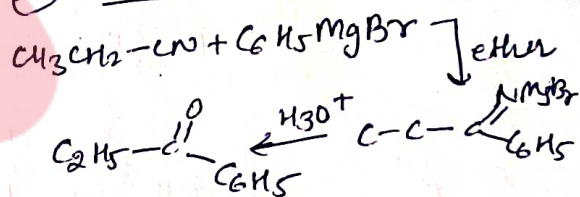
⑤ Gatterman Koch Reaction



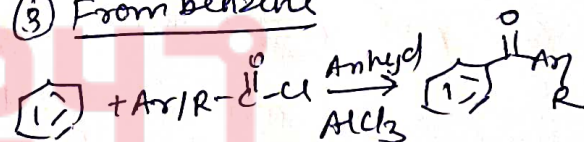
① From acyl chlorides



② From nitriles



③ From benzene



Physical properties

① State $\rightarrow$ Methanal is gas at room temperature. Ethanal is volatile liq. Other aldehydes are solid/liq at room temp.

② Boiling point $\rightarrow$ They have higher boiling point than hydrocarbons and ether.

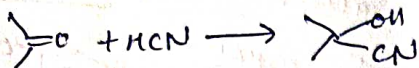
③ Solubility $\rightarrow$ Lower members of ald/ketone are soluble in water with inc in size of carbon chain solubility decreases. Though they are soluble in organic solvents.

Reactivity →

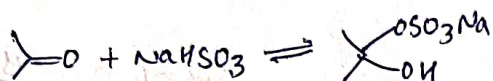
Aldehydes are more reactive than ketones both due to steric and electronic effect.

Nucleophilic Addition reaction

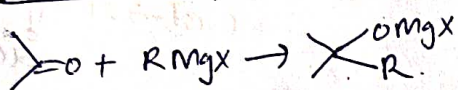
① Addition of HCN



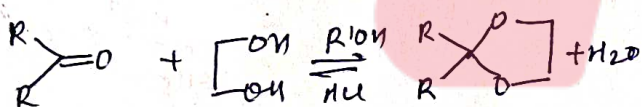
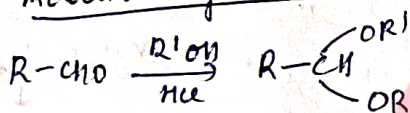
② Addition of $NaHSO_3$



③ Addition of Grignard reagent



④ Addition of alcohols

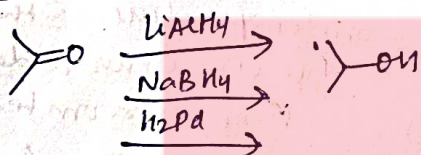


⑤ Addition of Ammonia

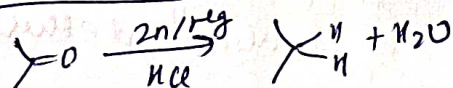


Reductions:

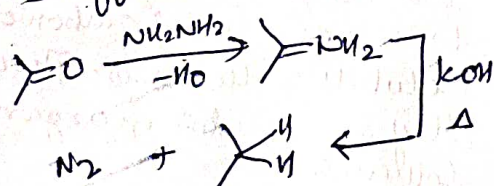
① Reduction to alcohols



② Clemmensen reduction

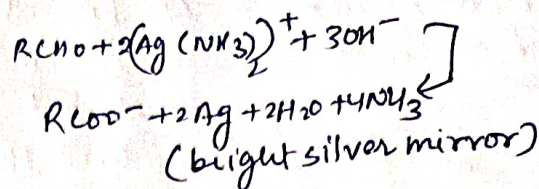


③ Wolff-Kishner reduction

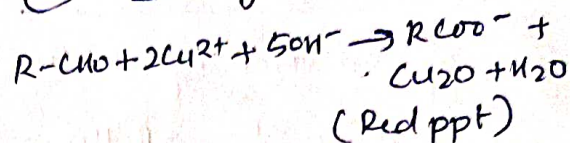


Oxidation :-

① Tollen's test

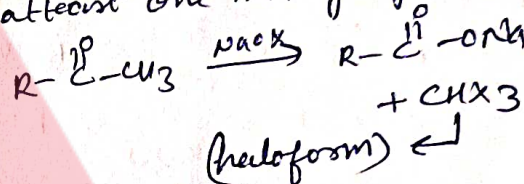


② Fehling's Test



③ Haloform reaction

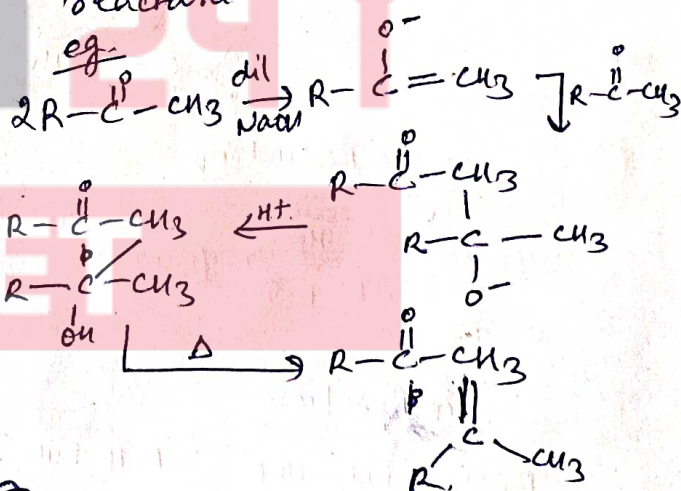
Reactant should contain atleast one methyl group.



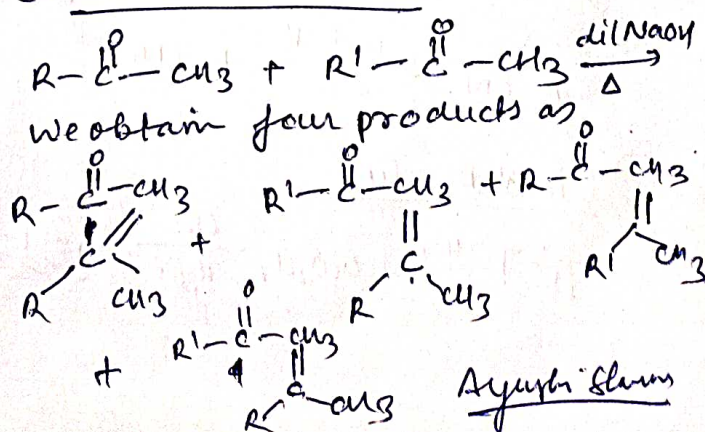
Name Reactions

① Aldol condensation

We obtain β -hydroxy aldehyde / ketone as product for aldehydes / ketones containing α H in reactant.

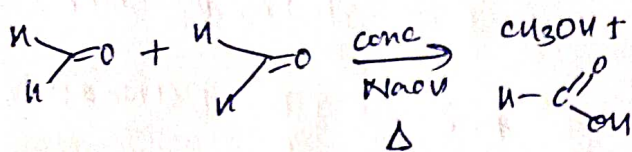


② Cross Aldol Reaction

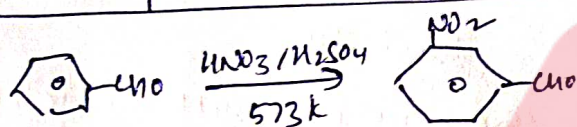


③ Cannizzaro Reaction

Aldehydes that do not have α -H undergo disproportionation reaction to give corresponding alcohol and acids

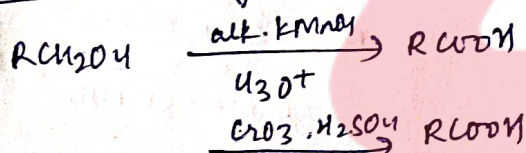


④ Electrophilic Substitution R^n

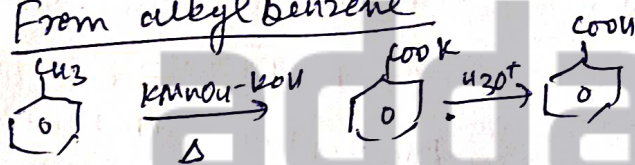


Preparation of Carboxylic acid

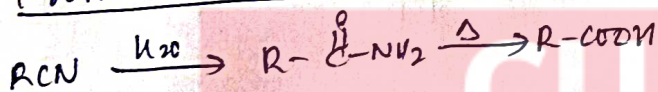
① From primary alcohol & aldehydes



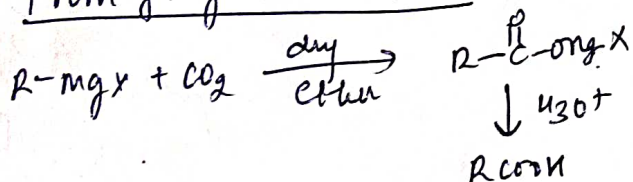
② From alkyl benzene



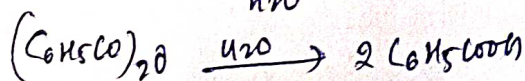
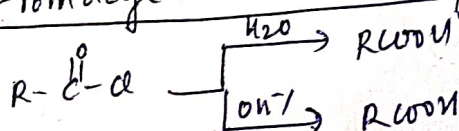
③ From nitriles and amides



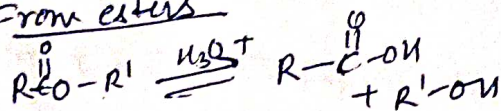
④ From grignard reagent



⑤ From acyl halide and anhydrides



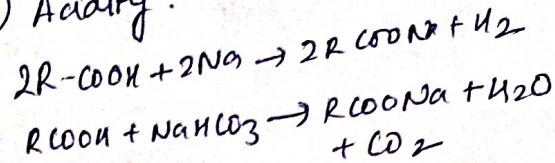
⑥ From esters



Reactions

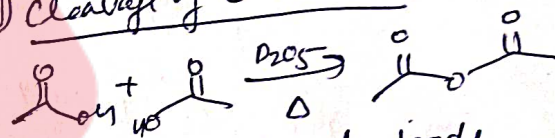
① Cleavage of O-H bond

a) Acidity.



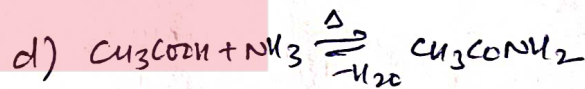
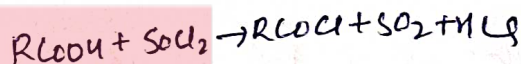
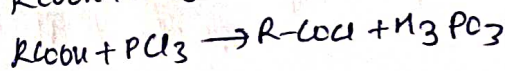
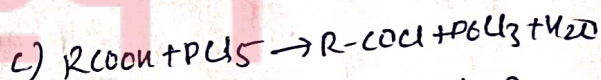
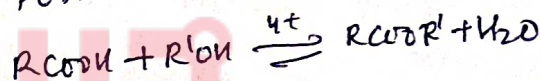
Acidic nature increases on attachment of Electron withdrawing group as they stabilize the anion formed on carbonyl carbon.

② Cleavage of C-OH bond

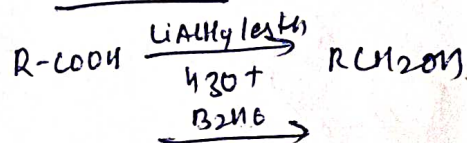


a) Formation of anhydride

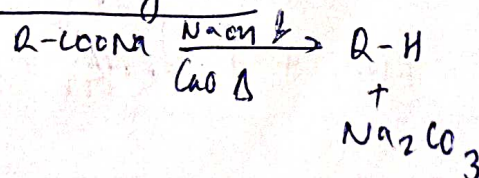
b) Formation of ester



③ Cleavage of Reduction

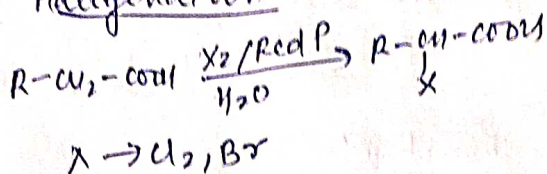


④ Decarboxylation

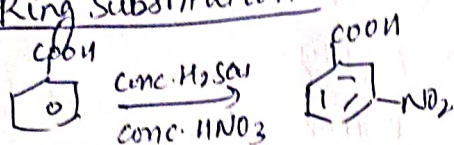


Acidic character

⑤ Halogenation



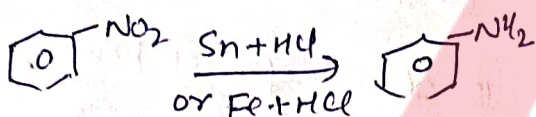
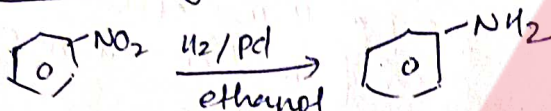
⑥ Ring Substitution



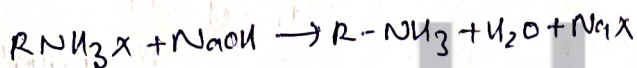
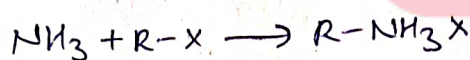
[AMINES]

Reactions of preparation

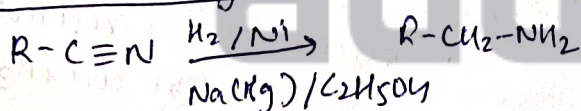
① Reduction of nitro compounds



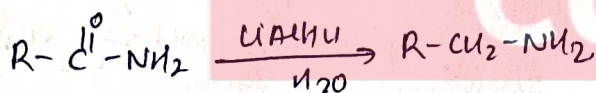
② Ammonolysis of alkyl halides



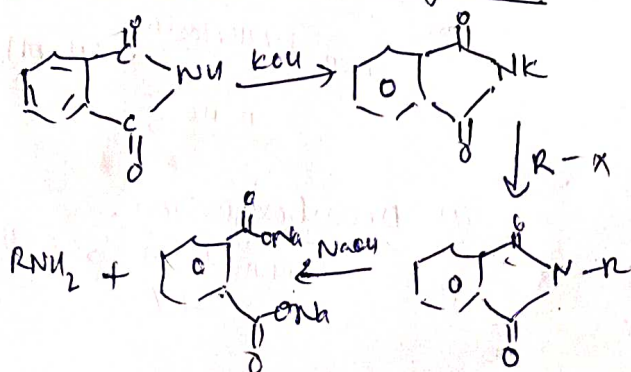
③ Reduction of nitriles



④ Reduction of amides



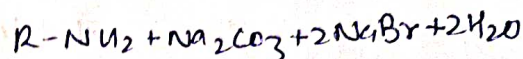
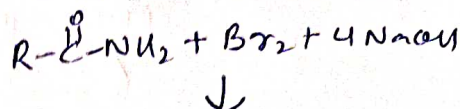
⑤ Gabriel phthalamide synthesis



NOTE

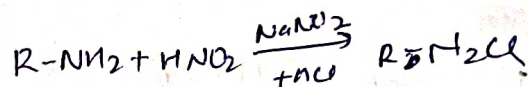
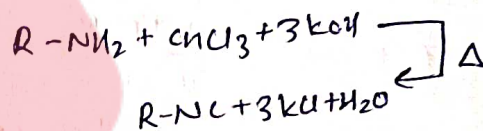
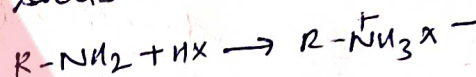
- only 1° amines can be prepared using this method.
- Aromatic amines cannot be prepared.

⑥ Hoffmann bromamide Degradation Reaction

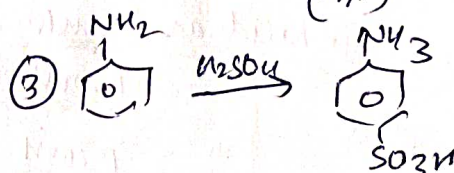
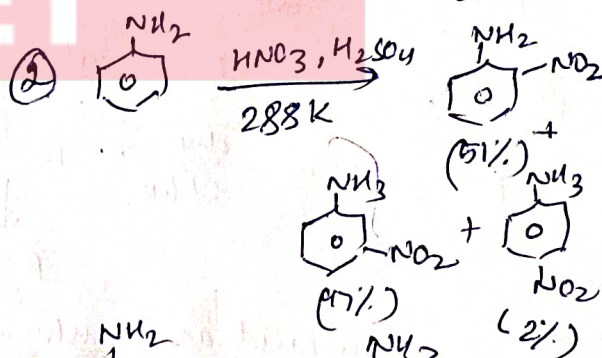
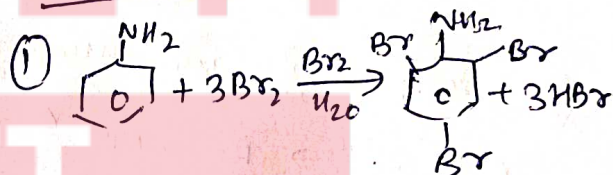


Basicity

Amines react with acid to form salts:-



Electrophilic Substitution R^n



[D & F Block]

- D block elements : Group 3-12
- They are known as transition elements due to their configuration $(n-1)d^{1-10} ns^{1-2}$

Properties

- All d-block elements are metals.
- All d-block elements are malleable, ductile, lustrous and sonorous except mercury which is liquid.

• Atomic Radii

Atomic radii decreases initially along the period till middle, then becomes constant and then increases.

• Ionic radii

It decreases with increase in oxidation state.

• Ionization enthalpy

As we move left to right across the group, ionization enthalpy increases as inter nuclear force of attraction increases.

- D-block elements exhibit variable oxidation states.

- D-block elements form complex and interstitial compounds.

- The magnetic moment of d-block elements increases with the increasing number of unpaired electrons.

- D-block elements show the formation of coloured complexes and alloys due to various charge transfer phenomena like d-d transition, LMCT, MLCT etc.

• F block elements

- General configuration $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$

• Lanthanoids :

Ce (Z=58) to Lu (Z=71)

Electronic configuration

$[Xe] 4f^{1-14} 5d^{0-1} 6s^2$

- They are highly dense metals, along with being soft, malleable & ductile.

- These metals have high melting points.

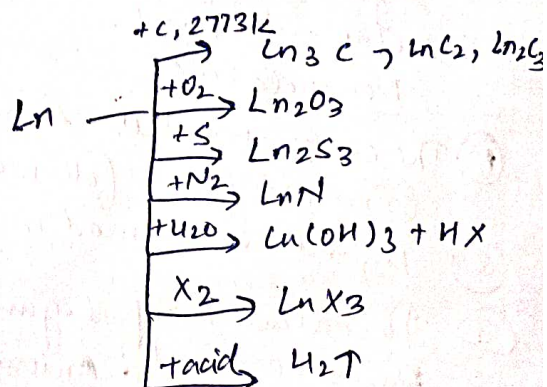
- Atomic radii → It decreases with increasing atomic number.

- Ionic radii → Also decreases with increase in atomic no.

- Lanthanoid contraction → This steady decrease in atomic and ionic radii is known as Lanthanoid contraction.

• Oxidation state

generally +3 but sometimes +2 and +4 also



Ayushi Sharma

COORDINATION COMPLEX

~~VBT~~ WERNER THEORY.

- (i) metal possess two types of valencies - ionizable (primary) and non-ionizable (secondary)
- (ii) Primary valencies are fulfilled by anions while secondary valencies are satisfied by negative/neutral molecules with lone pair.
- (iii) Double salt $\rightarrow$ when two or more salts are added to form a stable solid together and break into constituent ions when dissolved in water or any solvent. eg. Mohr salt.

A ligand is an ion/molecule that is bonded to central molecule in coordination entity. For eg. Cl^- , OH^- , CN^- etc. A ligand can be neutral or charged species.

Monodentate ligands $\rightarrow$ That ligate through one donor atom.

Bidentate ligands $\rightarrow$ That ligate through two donor atoms.

Polydentate ligands $\rightarrow$ That ligate through more than two donor atoms.

Ambidentate ligands $\rightarrow$ It is a ligand that contains two donor sites.

Coordination number $\rightarrow$ No. of ligands through which metal is bonded.

Nomenclature

- ① The cation whether simple or complex is named first followed by anion.
- ② Ligands are named in alphabetical order.
- ③ To indicate no. of ligands, numerical prefixes are used. Anionic ligands end in -o. Neutral ligands retain name & cationic end in -ium.

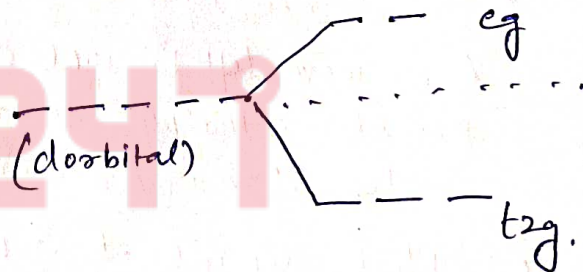
④ Coordination sphere is written in square bracket.

⑤ The naming of ligands is done in alphabetical order followed by metal ion and then the oxidation state of metal by a Roman numeral in parenthesis.

⑥ Name of coordination compound starts with small letter.

VBT

Two or more co-ordination compounds which have same molecular formula but have their ligands attached to the isomeric metal ions in different ways are known as isomers. The phenomena of different isomers is known as isomerism.



~~CFT~~

- ① Suitable no. of vacant orbitals must be present in the central metal ion for formation of coordinate bond with ligand.
- ② Central metal ion can use appropriate no. of s, p, d & f orbitals for hybridisation depending upon total no. of ligands.

Ayushi Sharma

③ The hybridised orbitals are allowed to overlap with those ligand orbitals that can donate an electron pair for bonding.

④ Outer orbitals or inner orbital complexes are formed depending whether outer d-orbitals or inner d-orbitals are used.

CFT

① Ligand is considered as point charge.

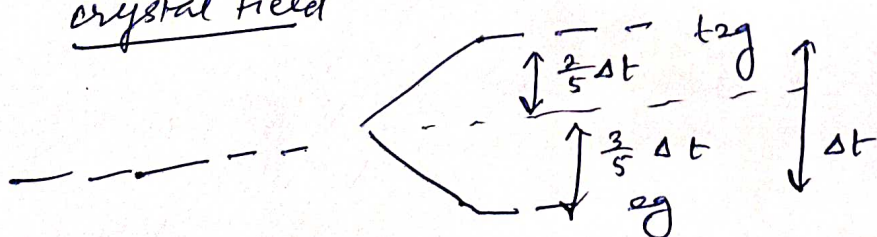
② Interaction is electrostatic in nature.

③ Metal ion is present at origin of axis. Ligands approach to metal ion along axis of octahedral complex between axis of tetrahedral complex and in the case of square planar complex four ligand approach to metal ion along x, y plane.

④ Due to interactions electron degeneracy of d-orbital is lost and splitting of d-orbitals occur.

⑤ Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d-orbitals.

d orbital splitting for tetrahedral crystal field



metal carbonyls
Homoleptic carbonyls are formed by d-block elements and contain carbonyl ligands only. eg. $V(CO)_6$, $Cr(CO)_6$ etc.

<u>Hybridisations</u>		<u>geometry</u>
C.No.	Hyb.	
4	sp^3	tetrahedral
4	dsp^2	square planar
5	sp^3d	trigonal bipyramidal
6	sp^3d^2	octahedral
6	d^2sp^3	octahedral

So $\propto$ strength of ligands.